

Article

External Reflection FTIR Spectroscopy Applied to Archaeological Pottery: A Non-Invasive Investigation about Provenance and Firing Temperature

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Abstract: The mineralogical composition of archaeological pottery is closely related to the raw material and the firing conditions, thus constituting a source of information both on the origin and the manufacturing technology of ceramic artefacts. The techniques used to clarify the composition of the ceramic material from the point of view of the mineralogical phases include X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR) and petrographic analysis. Such techniques normally require the taking of a sample from the object, thus often limiting their applicability to sherds rather than intact vessels. The present study aims to investigate the possibility of applying reflection FTIR spectroscopy in the mid- and near-IR to the non-invasive analysis of the mineralogical composition of archaeological pottery, with reference to a set of Etruscan ceramic materials from the excavation of Tarquinia (Italy).

Keywords: archaeological pottery; mineralogical phases; firing temperature; external reflection; FTIR spectroscopy; NIR spectroscopy; non-invasive analysis



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1. Introduction

The identification of mineralogical phases in the material of archaeological pottery vessels is a valuable tool for obtaining information on the raw material, and therefore on the origin, and on the manufacturing technology of the ceramics. In fact, some minerals, whether originally contained in the clay or intentionally added, for example, as temper, remain unchanged in the ceramic, while others derive from the transformation induced in the raw material by the firing conditions in terms of temperature and atmosphere [1]. Different experimental approaches are commonly applied to determine the mineralogical composition of ancient pottery. Petrographic analysis is especially suitable for the analysis of those ceramics that contain inclusions or rock fragments observable under an optical microscope [2], while X-ray powder diffraction (XRPD) enables the determination of the phase composition of both coarse and fine pottery [3]. Both techniques have been extensively used to study ancient ceramics since the 1970s and 1980s. More recent is the advent of the use of Fourier-transform infrared (FTIR) spectroscopy for the investigation of this important class of archaeological finds. It has been shown that this technique has the ability to provide the mineralogical fingerprint of the ceramic material, with the advantage over XRD of being able to identify both crystalline minerals and the pseudo-amorphous phases of the fired clay [4]. Among others, its application to authenticity studies of ancient ceramics has also been proposed [5].

All the techniques mentioned require a sample taken from the artifact, i.e., a fragment of at least 1 cm² for petrographic analysis and a few milligrams of powdered ceramic for XRPD and FTIR measurements, the latter being potentially less invasive than the former as

just 1 mg of powder may be sufficient for the analysis [2,4]. It should, however, be noted that even if a small amount of material can be used for one or the other analysis, the sample cannot in principle be too limited as it must be representative of the whole. This fact is an obvious limitation when an intact vessel needs to be examined and sampling should be avoided.

External reflection FTIR spectroscopy makes it possible to analyze samples in a non-invasive manner and, in principle, to investigate artifacts in situ by means of portable instrumentation. It has therefore found an important field of application in cultural heritage, as regards, for example, the identification of pigments [6–8], binders [8,9] and surface alteration products [10] in paintings, plastics in museum collections [11,12], varnishes [13], gemstones [14], etc. Mid-IR (MIR) ($4000\text{--}400\text{ cm}^{-1}$) is the spectral range usually exploited in these measurements; however, due to the higher extinction coefficients of the absorptions falling in this interval, it is also the region where the bands observed are more likely to be distorted [15,16]. For this reason, the usefulness of reflection spectra acquired in the near-IR (NIR) region ($13,000\text{--}4000\text{ cm}^{-1}$) has been highlighted, in particular for the identification of those compounds which, containing in their molecular structures N-H, O-H and C-H functional groups, give rise to overtone and combination vibrational bands in this region. Being weaker than the fundamental ones, these bands are less prone to distortions in the reflection spectra [16]. In the field of cultural heritage, external reflection spectra acquired non-invasively in the NIR region have been exploited above all in the investigation of inorganic pigments containing OH groups or H₂O molecules [6,7] and of organic binders for painting [9,17]. As regards archaeological materials, the application of the technique in its macroscopic version, i.e., the one that can be applied in situ, has been rather limited to date, with few examples mainly concerning the surface decoration of ancient pottery [18,19].

The present work aimed to investigate the possibility of non-invasively studying the mineralogical composition of archaeological ceramics via external reflection FTIR spectroscopy with the use of portable instrumentation. With a view to a possible transfer of the method to intact vases, in the present study, the technique was applied to sherds of fine pottery and bucchero from the Etruscan city of Tarquinia (central Italy) dating back to the 8th–6th century B.C., which had already been examined with laboratory techniques (XRD and transmission FTIR) for the determination of their mineralogical composition [20,21]. In this way, comparison data were available to verify the reliability of those obtained from external reflection FTIR measurements. Both the MIR region, where the bands of most of the minerals of interest can be found, and the longer wavelength part of the NIR were considered, the latter in particular to obtain information on the firing temperature as already proposed by one of the authors for diffuse reflectance measurements on powder samples [20].

2. Materials and Methods

2.1. Archaeological Ceramic Samples

Tarquinia (province of Viterbo, Italy) is an important archaeological site of the Etruscan civilization, known above all for the painted tombs of its necropolis, part of the UNESCO heritage. In addition to the necropolis, the site also includes the excavations of the ancient city, in the site called Civita, with the remains of the temple known as Ara della Regina and of the so-called monumental complex, the center of political and religious life. These excavations are conducted by the archaeologists of the “Progetto Tarquinia” of the University of Milan (Milan, Italy).

Tarquinia has been recognized as an important production center for pottery in the Etruscan context [22,23]. The sherds examined in the present work belong to the two classes of fine ware and of the so-called bucchero. The class of fine pottery includes several sub-classes according to the characteristics of its decoration: plain white or banded, when the decoration was absent or consisted only of colored stripes; Etrusco-geometric, with rationally ordered decorative motifs; Etrusco-Corinthian, with figured decoration; black

gloss, characterized by a lustrous black coating, covering the surface in whole or in part. Bucchero is instead a typical Etruscan ceramic characterized by a homogeneous black or grey color both on the surface and in the body.

Table 1 lists the pottery sherds analyzed in the present work.

Table 1. List of the ceramic samples from the Civita di Tarquinia examined via external reflection FTIR spectroscopy in this work, with their class and chronology. For the distinction between local and imported bucchero samples, see text. Legend: n.a. = not available.





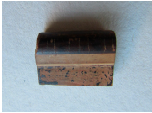
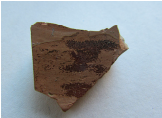









Sample		Class	Chronology (Century B.C.)
80/25		Etrusco-geometric	8th–7th
274/7		Etrusco-geometric	8th–7th
186/2		Etrusco-Corinthian	6th first half
227/35		Etrusco-geometric	8th–7th
3/612		Etruscan black gloss (archaic)	6th onwards
170/2		Etrusco-Corinthian	6th first half
3/73		Etruscan black gloss (archaic)	6th onwards
3/607		Etruscan black gloss (archaic)	6th onwards
199/3		Etrusco-Corinthian (or Corinthian)	8th–7th
12/163		Bucchero (local production)	7th–6th first half

Table 1. Cont.

Sample		Class	Chronology (Century B.C.)
845/2	n.a.	Bucchero (local production)	7th last quarter–6th first quarter
437/122		Bucchero (local production)	7th third quarter
125/22		Bucchero (local production)	6th first half
779/1		Bucchero (local production)	7th third quarter
197/6		Bucchero (imported)	7th second half
763/1		Bucchero (imported)	7th last quarter–6th first quarter
681/49		Bucchero (imported)	7th last quarter
663/2		Bucchero (imported)	7th last quarter
Ac10/23		Bucchero (imported)	7th last quarter–6th first quarter

Most of the nine fine ceramics of the Etrusco-geometric, Etrusco-Corinthian and black-gloss subclasses had been previously recognized as locally produced based on their elemental composition [23]. A possible exception is sample 199/3, which, as discussed below, has a slightly different mineralogical composition from the other samples in the relative quantities of the observed phases, and had been assumed by archaeologists to be of Corinthian production from the stylistic point of view. As already reported by the authors in reference [20], all these samples lie, however, in the quartz–diopside–anorthite phase field within the so-called “ceramic triangle” $\text{CaO} + \text{MgO}/\text{Al}_2\text{O}_3/\text{SiO}_2$. It has therefore been verified that the main difference in their mineralogical composition derives from the different firing temperatures [20].

Instead, as regards the ten bucchero samples, for five of them, a local production has been previously recognized based on elemental analysis, while the remaining five samples are considered on the same basis as imported to Tarquinia from other Etruscan centers, probably from Cerveteri [21]. At the same time, a similar firing temperature, not exceeding 800 °C, was estimated on the basis of FTIR and NIR spectroscopic data for all these bucchero samples [21]. For these fragments, therefore, it is assumed that the differences in the mineralogical composition derive mainly from the different origin and, consequently, from the different composition of the raw material.

2.2. Instrumental Methods

External reflection FTIR spectra were acquired using a Bruker Alpha spectrometer, equipped with a specular reflection accessory that enables contactless measurements at near-normal incidence. The spectrometer is completely portable, as a result of its compact dimensions ($30 \times 20 \times 15$ cm) and low weight (7 kg) and can therefore potentially be easily used in museum spaces. Spectra were collected in the $7500\text{--}375$ cm^{-1} range with 4 cm^{-1} resolution. A number of scans ranging from 200 to 400 were summed (corresponding to an acquisition time of 4–8 min), depending on the signal-to-noise ratio obtainable from the surface of each sample. The measurement area, a circular spot with a diameter of approximately 0.6 cm, could be selected using an integrated video camera. For all sherds, the side corresponding to the external surface of the original vessel was examined to simulate the situation corresponding to the analysis of an intact vase, and areas without decoration were, of course, chosen for the measurements. When allowed by the extension of the undecorated area, replicate measurements were performed on each sample to check the reproducibility of the spectral data. In all cases, the best obtained spectrum was chosen for discussion. The Kramers–Kronig transform was applied to the reflectance data in the MIR region, while in the NIR interval, the $\log(1/R)$ function was used. A preliminary study of the possible effect of the radius of curvature of the ceramic surface on the reflection IR spectral pattern was carried out on modern unglazed ceramic vessels (Fornace Curti, Milan, Italy) of different shapes but with the same raw material and firing conditions. As shown in Figure S1 (Supplementary Material), the spectra acquired on different parts of the vessels (e.g., the curved wall or the flat bottom) were satisfactorily reproducible.

The transmission FTIR spectra on KBr pellets, diffuse reflectance NIR spectra and powder XRD patterns, which will be used below for comparison, were acquired both for fine ware and bucchero samples as described, respectively, in references [20,21]. It should be emphasized that the ceramic powder used for these measurements was taken from the pottery fragments after having removed the outermost layer with a diamond tip.

3. Results and Discussion

3.1. Fine Ceramics

The external reflection FTIR spectra obtained for the Tarquinia fine pottery samples (Figure 1, left) are all characterized by the typical absorptions around 1070 and 480 cm^{-1} , associated with the stretching and bending modes of Si–O bonds of fired clay [4]. These absorptions dominate the reflection as well as the corresponding transmission FTIR spectra of the samples (Figure 1, right).

Furthermore, the characteristic doublet at 798 and 780 cm^{-1} due to quartz SiO_2 can also be observed [4], together with a component of the Si–O stretching band around 1124 cm^{-1} attributable to same mineralogical phase. This latter absorption appears as a shoulder for all the fragments, with the exception of samples 3/73 and 3/607, for which it is the main component of the band, and for sample 199/3, for which it is less easily distinguishable. As reported in Table 2, the XRD data available for these samples confirm that for the ceramic 199/3, the quantity of quartz is relatively lower than for the other phases.

Another common characteristic of the spectra of all the sherds are the fundamental bands of calcite CaCO_3 at around 1430 and 875 cm^{-1} [4]. For this phase, some significant differences with the transmission spectra of the same samples can be detected. First of all, for the two Etruscan geometric pottery fragments 80/25 and 227/35, the bands due to calcite are particularly evident in the corresponding transmission spectra, while they are extremely weak, relative to the Si–O stretching band, in the external reflection spectra. This is not unexpected, as it has been shown that, in the reflection IR spectra obtained from mat surfaces, the bands with the highest absorption coefficients lose spectral contrast, becoming less evident for rough surfaces with particle size comparable with the wavelength of infrared radiation. In this case, in fact, the volume reflection, i.e., the component of light that has penetrated the material before being reflected, is the dominant one, and the intensity of this component decreases as the absorption coefficient increases [15,16].

This phenomenon is relatively less significant for combination and overtone bands, which have lower absorption coefficients, and, therefore, these bands gain in intensity with respect to fundamental ones. Correspondingly, in the MIR reflection spectra obtained in the present work for Tarquinia pottery, the band of calcite around 2500 cm^{-1} , deriving from the combination of the asymmetric and symmetric stretching modes of the CO_3^{2-} anion [6], can be easily observed with an intensity comparable with that of the fundamental band at 1430 cm^{-1} (Figure 1, left) and becomes an important marker of the presence of this phase in the ceramic material. Another relevant difference between the reflection and transmission spectra of the sherds examined lies in the fact that the bands due to calcite are detected in reflection for eight out of ten samples, while they are present in the transmission spectra for only two of them, 80/25 and 227/35 (Figure 1a,d, right). For sample 274/7, the transmission spectrum was not available, but its abundant content of calcite was confirmed using XRD data (Table 2). In principle, two possible reasons could be identified for this discrepancy between the reflection spectra obtained on the surface of the intact fragments and transmission spectra acquired from the ceramic powder taken from them after the removal of the outer layer (as explained in Section 2.2). The first one is possible contamination from the burial soil, which is typically calcareous in the site of Tarquinia. The ancient city is, in fact, located on the top of a hill formed by “macco”, made up of fossiliferous calcarenite and cemented bioclastic sands [24]. However, this hypothesis is at least partially contradicted by the results obtained on bucchero samples; as discussed below, in that case, the imported materials, obtained from a non-calcareous clay, did not show reflection IR bands associated with calcium carbonate, although they too have been found in the excavations of Tarquinia. The second possible reason must be sought in the fact that the samples of fine ceramics investigated here were almost all obtained with the local calcareous clay [20], and thus, even when fired at temperatures higher than the decomposition temperature for calcium carbonate ($700\text{--}800\text{ }^\circ\text{C}$), they contain mineralogical phases that can decompose into calcite especially if buried in humid conditions [25,26], as will be detailed below. Apparently, therefore, for those samples for which the presence of calcite is evidenced only by reflection FTIR spectra, it can be hypothesized that the decomposition phenomenon has affected only the outer layer of the ceramic material (in the order of a few micrometers, the average penetration depth of radiation in the mid-IR), obviously more exposed to humidity and acid substances from soil than the bulk, especially if the latter is not very porous.

Besides the common features discussed above, the reflection IR spectra of the fine ware fragments from the Civita di Tarquinia also show some relevant differences. The most evident one is the appearance of a shoulder on the low-wavenumber side of the Si-O stretching band, at around 950 cm^{-1} , for the Etrusco-geometric sample 227/35 (Figure 1d, left), the Etrusco-Corinthian samples 170/2 and 199/3 (the latter possibly Corinthian) (Figure 1f,i, left), and the black-gloss samples 3/612, 3/73, and 3/607 (Figure 1e,g,h, left). This component is perhaps present, but not so evident, in the spectrum of the Etrusco-Corinthian sherd 186/2 as well (Figure 1c, left). However, this spectrum shows a certain distortion of the absorption bands, not even removed by the application of the Kramers–Kronig transform and probably due to the morphological characteristics of the surface, therefore recalling one of the possible limitations of the technique, the quality of the results of which obviously depends on the features of the surface itself. Together with the band at 950 cm^{-1} , three characteristic signals are observed at lower wavenumbers for the same ceramics, at 618, 573 and 540 cm^{-1} , and can be assigned to anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$ [27]. The band at 950 cm^{-1} is consequently attributable to the same mineralogical phase [27], but a minor contribution to it by diopside $\text{CaMgSi}_2\text{O}_6$, characterized by an absorption at 965 cm^{-1} [28], cannot be excluded. Corresponding bands are observed in the transmission FTIR spectra of the same samples (Figure 1, right), albeit with a shift in the signal due to Si-O stretching of the feldspar from 950 to 930 cm^{-1} . The presence of appreciable quantities of anorthite in these materials is confirmed using XRD data (Table 2). Only for the possibly Corinthian pottery 199/3, characterized by high amounts of both anorthite and diopside

(Table 2), can the bands due to the Si-O stretching modes of the latter phase be clearly distinguished in the transmission spectrum at 967 and 868 cm^{-1} [28]. In the previous study of fine pottery from Tarquinia [20], the observation of these mineralogical phases had been related to the firing of calcareous clay at temperatures ranging from 850 to 1000 $^{\circ}\text{C}$, with lower temperatures in this range observed for Etrusco-geometric pottery and higher values for Etrusco-Corinthian and black-gloss pottery. In fact, in the set of samples examined in the present work, the only Etrusco-geometric ceramic showing the 950- cm^{-1} band in its reflection spectrum is sample 227/35 (Figure 1d, left), which, on the basis of XRD data, contains anorthite, diopside and also gehlenite (Table 2), from whose decomposition the secondary calcite abundantly present in this sample most likely derives [25]. From a general point of view, the calcite also detected for the other samples in the reflection FTIR spectra can be due to the incipient decomposition of these silicate phases in a humid burial environment [25,26]. For the other two fragments of Etrusco-geometric pottery, 80/25 and 274/7, only the bands due to calcite and quartz, besides fired clay, are observed in the reflection FTIR spectra (Figure 1a,b, left), similarly to the corresponding transmission spectra (Figure 1a,b, right) and consistently with XRD data (Table 2). For these samples, therefore, a firing temperature lower than 800 $^{\circ}\text{C}$ of a still calcareous clay can be assumed based on the IR reflection data.

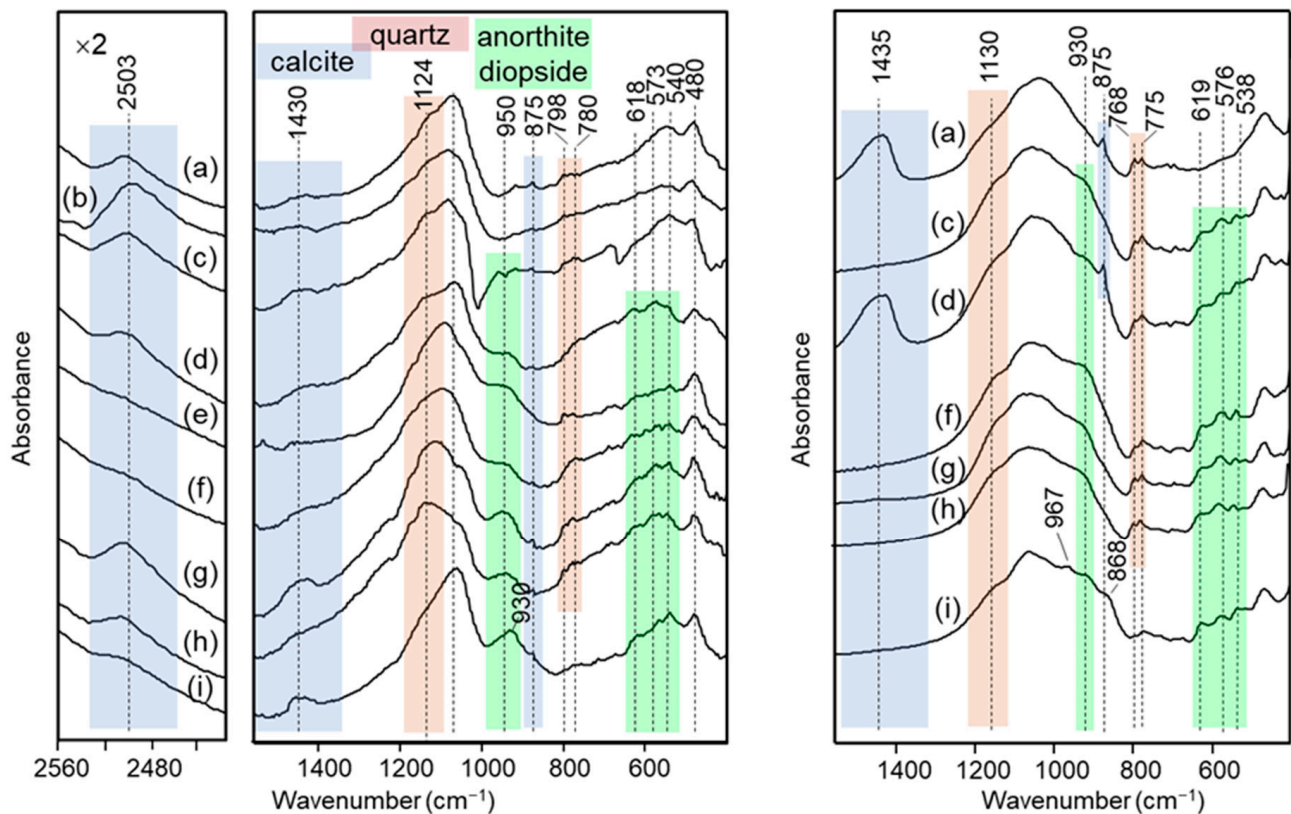


Figure 1. (Left) External reflection FTIR spectra on intact sherds and (right) transmission FTIR spectra on KBr pellets of samples: (a) 80/25 (Etrusco-geometric); (b) 274/7 (Etrusco-geometric); (c) 186/2 Etrusco-Corinthian); (d) 227/35 (Etrusco-geometric); (e) 3/612 (black-gloss); (f) 170/2 (Etrusco-Corinthian); (g) 3/73 (black-gloss); (h) 3/607 (black-gloss); (i) 199/3 (Etrusco-Corinthian). The bands due to calcite, quartz and the silicates anorthite and diopside are highlighted in blue, light red and green, respectively. The part of the spectra where the combination band of calcite at 2504 cm^{-1} is found (left box) has been expanded in intensity by a factor of 2. Note: transmission FTIR spectra were not available for samples 274/7 and 3/612.

Table 2. Mineralogical phases recognized by XRD in the ceramic paste of the fine ware samples from the Civita di Tarquinia. Peak intensity: +++++ = very strong, +++ = strong, ++ = medium, + = weak, t = traces, - = not found.

Sample	Mineralogical Phases								
	Albite	Analcite /Wairakite	Anorthite	Calcite	Diopside	Hematite	Gehlenite	Muscovite	Quartz
80/25	+	-	-	+++	-	-	-	+	++++
274/7	+	-	-	+++	-	-	-	+	++++
186/2	-	-	++	-	++	+	-	-	++++
227/35	-	-	+	+++	+	+	t	-	++++
3/612	-	-	++	-	+	+++	+	-	++++
170/2	-	-	+++	-	++	+	-	+	++++
3/73	-	-	+++	-	++	+++	-	-	++++
3/607	-	-	+++	-	++	+++	-	-	++++
199/3	-	++	++++	-	++++	-	-	-	+++

In reference [20], the hypotheses on the firing temperature of the fine ware samples from the Civita di Tarquinia could be checked by comparing the intensities of the bands due to absorbed water and, possibly, to the residual OH groups in the diffuse reflectance NIR spectra of the ceramic powders in the range 1300–2500 nm, where combination and overtone bands of the O-H bond vibrations are located [29,30]. In the present work, it was therefore decided to verify whether the NIR portion of the external reflection FTIR spectra acquired on the intact sherds could be used for the same purpose. As detailed in Section 2.2, the part of the NIR spectral region nominally accessible through the portable spectrometer adopted for the non-invasive measurements ranges from 7500 to 4000 cm^{-1} , i.e., from about 1350 to 2500 nm. Of course, in the analyses performed on the surfaces of the fragments via external reflection rather than on powders via diffuse reflection, the signal-to-noise ratio may not be as good but, nevertheless, it was possible to observe for all samples the band at about 5200 cm^{-1} (1900 nm) due to a combination of the stretching and bending modes of the water molecule [29,30] (Figure 2, left).

Consistently with the diffuse reflection NIR spectra of the same ceramics (Figure 2, right), the highest intensity of the above band is observed for the Etrusco-geometric samples 80/25 and 274/7, i.e., those for which the lower firing temperature has been hypothesized based on the mineralogical composition. The band is weaker for sample 227/35 (Figure 2c, left), also Etrusco-geometric, for which a firing temperature higher than 800 °C was indeed assumed due to the detection of the silicate phases (anorthite, diopside and gehlenite) formed from the reaction of CaO (and MgO) deriving from the decomposition of carbonates with SiO_2 resulting from the decomposition of clay minerals [25]. The presence of gehlenite indicated a coarser particle size of the raw material, as it is formed at the grain boundaries [31], but also to a firing temperature not as high as that of the samples which will be discussed below, preventing its complete transformation into anorthite via a further reaction with SiO_2 [25]. In agreement with this consideration, the Etrusco-Corinthian ceramic 186/2 and the black-gloss ceramics 3/612, 3/73 and 3/607 showed the lower intensity for the combination band of water in their NIR spectra, both in external and diffuse reflectance (Figure 2d–g). In fact, as already discussed in reference [20], for their more recent chronology (Table 1), the ceramics belonging to these subclasses of fine pottery were produced with a more refined technology, both from the point of view of the raw material and the firing temperature. In the case of black-gloss pottery, moreover, a higher temperature must also be reached to ensure the sintering of the black coating formed in the reducing step of the firing to avoid its re-oxidation during the subsequent oxidizing one [32]. Both in the external reflectance and diffuse reflectance spectra, a shift in the

maximum of the combination band can be observed, respectively, from 5213 to 5240 cm^{-1} and from 5204 to 5235 cm^{-1} , when passing from a higher to a lower water content. This is probably due to the fact that, in the first case, both free and associated H_2O molecules are present, while in the second, fewer isolated molecules are responsible for the band [29,30]. In fact, water molecules involved in strong hydrogen bonds give rise to a shoulder at lower wavenumbers (typically around 5050 cm^{-1} [29]), and thus to the asymmetry and, presumably, also to the lower wavenumber of the maximum of the considered band.

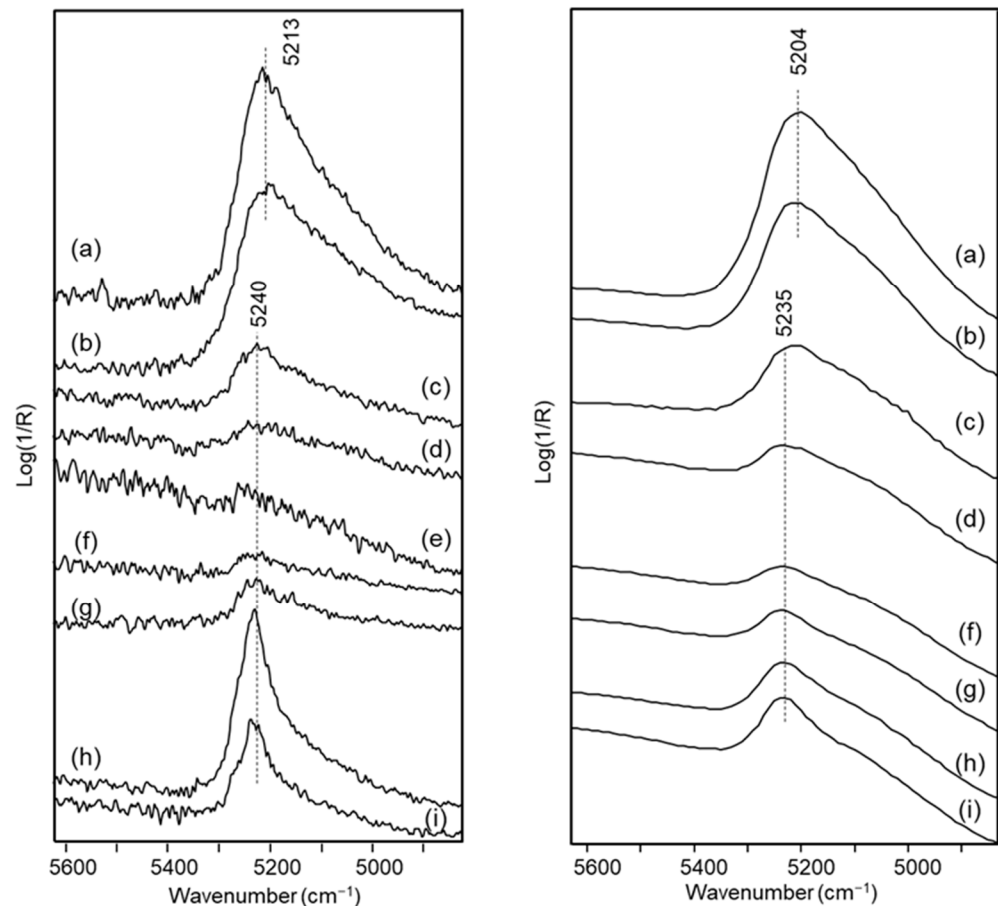


Figure 2. (Left) External reflection FTIR spectra on intact sherds and (right) diffuse reflectance spectra on powdered ceramic in the NIR region of samples: (a) 80/25 (Etrusco-geometric); (b) 274/7 (Etrusco-geometric); (c) 227/35 (Etrusco-geometric); (d) 186/2 Etrusco-Corinthian); (e) 3/612 (black-gloss); (f) 3/73 (black-gloss); (g) 3/607 (black-gloss); (h) 170/2 (Etrusco-Corinthian); (i) 199/3 (Etrusco-Corinthian). Note: the diffuse reflectance NIR spectrum was not available for sample 3/612.

A different situation occurs for the Etrusco-Corinthian ceramic 170/2 and the supposed Corinthian ceramic 199/3. In fact, in the NIR diffuse reflectance spectra, the combination band has a relatively low intensity and a shape comparable with that observed for the other samples (Figure 2h,i, right), consistently with the firing temperature above 800 °C that can be assumed for these sherds based on their mineralogical composition, as indicated by both external reflection and transmission FTIR spectra (Figure 1f,i) and XRD data (Table 2). Instead, in the NIR external reflectance spectra acquired on the intact sherds, a sharper and more intense band is detected for both samples at 5240 cm^{-1} (Figure 2h,i, left). The shape and position of the band closely resembles those observed for water molecules in minerals belonging to the zeolite family [33], an assignment suggested by the XRD data (Table 2), which, at least for the paste of sample 199/3, show a consistent amount of analcime $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$, or wairakite $\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$, indistinguishable from the former based on XRD [25,26]. However, both phases are considered alteration products

formed from gehlenite upon reaction with H_2O and CO_2 [25,26]. Based on NIR spectra, apparently one or the other of the two phases is present both in the body and the surface of the ceramic 199/3, while in the case of sample 170/2, for which they are not detected via the XRD analysis of the powdered ceramic, the hypothesis of a more superficial deterioration should be taken into account, similarly to that discussed above for calcite detected in external reflection MIR spectra of samples fired above the decomposition temperature of calcium carbonate.

3.2. Bucchero Ware

Figure 3 shows the MIR external reflection spectra and, for comparison, the transmission spectra of the bucchero sherds from the excavations of the Civita di Tarquinia examined in the present work and listed in Table 1.

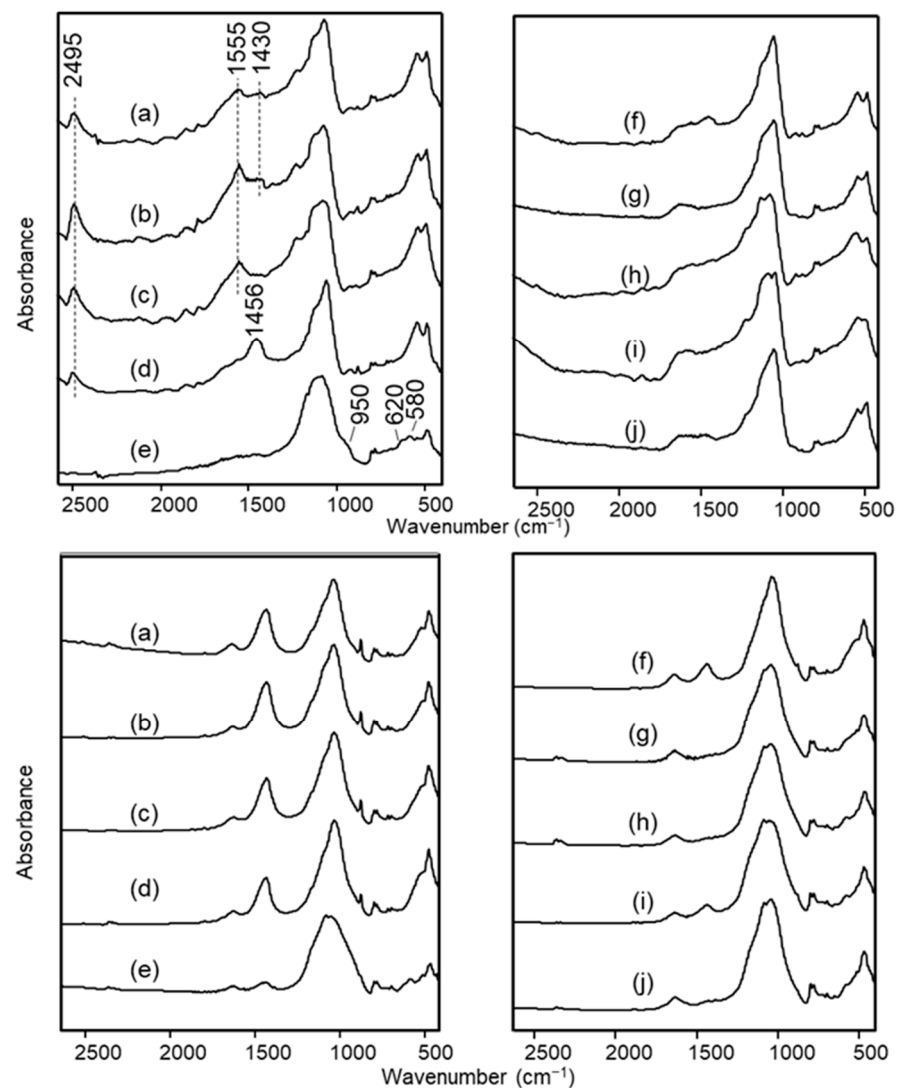


Figure 3. (Top) External reflection FTIR spectra on intact sherds and (bottom) transmission FTIR spectra on KBr pellets of locally produced bucchero samples (a) 12/163, (b) 845/2, (c) 437/122, (d) 125/22, (e) 779/1, and of imported bucchero samples (f) 197/6, (g) 763/1, (h) 681/49, (i) 663/2, (j) Ac10/23.

It is evident that the two groups of bucchero, previously identified as locally produced and, respectively, imported to Tarquinia from other Etruscan centers (see Section 2.1) [21], show two well-distinguishable MIR spectral patterns when examined in external reflection mode (Figure 3, top), and that these patterns have a good match with those obtained

in transmission mode for the powdered ceramics (Figure 3, bottom). In particular, for four of the five local materials, with the exception being represented by sample 779/1, which will be discussed later, the spectra only show bands due to fired clay, quartz and, finally, calcite (Figure 3a–d). The characteristic absorptions of this last phase are instead absent in the spectra of the imported bucchero ceramics (Figure 3f–j). However, since for these samples no other signals possibly attributable to calcium-containing phases formed during firing were found, it can easily be concluded that these bucchero ceramics were not produced from a calcareous clay and are therefore not of local origin. In this regard, a useful comparison is the FTIR reflection spectrum of the local bucchero 779/1 (Figure 3e, top). In this spectrum, the absorptions due to calcite are also absent, but the band at around 1070 cm^{-1} corresponding to the Si-O stretching modes is broader than for the other samples, both local and imported, and a shoulder at around 950 cm^{-1} is observed together with the bands between 650 and 500 cm^{-1} , which, in Section 3.1 were assigned to anorthite. Bucchero 779/1 was thus produced from a calcareous clay, in line with its local origin, but at a temperature higher than the other samples, which favored the decomposition of calcite and the formation of calcium silicates. These results are in good agreement with the mineralogical phases detected via the XRD analysis of powders from some of the bucchero samples examined here (Table 3).

Table 3. Mineralogical phases recognized by XRD in the ceramic paste of the bucchero samples from the Civita di Tarquinia [21]. Peak intensity: ++++ = very strong, +++ = strong, ++ = medium, + = weak, t = traces, - = not found.

Sample	Mineralogical Phases							
	Albite	Anorthite	Calcite	Diopside	Microcline	Muscovite	Orthoclase	Quartz
12/163	+	-	+++	-	-	t	t	++++
845/2	+	-	+++	-	-	t	t	++++
437/122	t	t	++	-	-	t	-	++++
125/22	+	-	++	-	-	+	-	++++
779/1	t	+	t	t	-	-	-	++++
763/1	t	-	-	-	-	t	t	++++
681/49	+	-	-	-	t	t	t	++++
Ac 10/23	t	-	-	-	-	t	t	++++

In conclusion, it is worth taking a closer look at the calcite bands observed in the external reflection FTIR spectra of the local bucchero samples. Similarly to what has already been discussed for fine pottery (Section 3.1), the fundamental bands of this phase are quite weak, especially when compared with the corresponding transmission FTIR spectra, while the combination band at around 2500 cm^{-1} has an intensity comparable to them. Furthermore, the band assigned to the asymmetric stretching of the CO_3^{2-} ion is located at 1555 cm^{-1} for bucchero samples 12/163, 845/2 and 437/122 (Figure 3a–c, top), with a shoulder at 1430 cm^{-1} for the first two, while for bucchero 125/22, a more evident band with a rounded top is observed at 1456 cm^{-1} (Figure 3d, top). A similar variation has been reported in the literature for plasters when passing from sparitic to micritic limestone [34], suggesting that, in sample 125/22, calcite has a smaller crystal size than in the other local bucchero samples. Interestingly, in reference [21], bucchero 125/22 turned out to be part of a group of local samples with a slightly different elemental composition from the more numerous one, similar to those that K. Burkhardt hypothesized to be produced in Tarquinia but with a different raw material, coming, for example, from the sediment of the nearby Marta river [35]. Possibly, the difference detected in the IR external reflection spectra could also be ascribed to the same reason.

4. Conclusions

The present work aimed to be a preliminary investigation of the possible application of external reflection FTIR spectroscopy, by means of a portable spectrometer, to the non-invasive and, in perspective, in situ study of the mineralogical composition of archaeological ceramic objects.

The possibility of obtaining reproducible spectra from ceramic materials with a different shape (and curvature radius of the surface) but identical raw material and firing conditions was first tested with satisfactory results on unglazed ceramic vessels from a modern manufacturer.

The application of the technique to a set of fragmentary fine ceramics from the excavations of the Etruscan site of Civita di Tarquinia then demonstrated that FTIR spectra acquired in external reflection mode are just as informative as those acquired in transmission mode for powder samples taken from the same ceramics. In particular, the reflection spectral patterns characteristic of ceramics obtained by firing at different temperatures a calcareous clay, like that available in the Tarquinia area, were clearly indicated. Among the different mineralogical phases characterizing this typology of ceramic material, it was highlighted that calcite can be better recognized, in the reflection spectra, thanks to its combination band at around 2500 cm^{-1} , as the fundamental ones at 1430 and 875 cm^{-1} are rather weak due to the prevalence of volume over surface reflection. Furthermore, in the reflection spectra of those ceramic samples fired at temperatures higher than the decomposition temperature of calcium carbonate, it was possible to clearly detect bands associated with calcium silicates which form during firing, especially anorthite. The variation in the firing temperature within the set of samples considered, as suggested by the variability in the mineralogical composition indicated by the reflection spectra (and confirmed by XRD data that were available for these samples), could be verified thanks to a combination band located in the NIR portion of the reflection spectra, between 5240 and 5210 cm^{-1} , and attributable to absorbed H_2O molecules. As previously observed for NIR diffuse reflectance spectra acquired for powder samples taken from these ceramics and others of the same classes, in fact, the intensity of this band decreases parallel to the increase in the firing temperature. Therefore, a single non-invasive measurement in external reflection with the portable spectrometer, covering both the MIR and part of the NIR spectral region, allows to obtain both the information relating to the mineralogical composition and that relating to absorbed water, which can be combined to estimate the variation in the firing temperature within a set of ceramic objects. Further information obtained in these measurements relates to the presence of decomposition products of the silicate phases which form during firing, such as calcite and wairakite (or analcime), that can be observed in the outer layer of the ceramic material even when they are not significantly present in the bulk of the material itself.

The investigation conducted with the same technique on a series of bucheri from the same archaeological site confirmed that the external reflection FTIR spectra match satisfactorily with those obtained in transmission from powder samples, thus reinforcing the reliability of the non-invasive approach. Furthermore, it was possible to clearly distinguish, from these spectra, the bucheri produced locally with the typically calcareous clay from those imported to Tarquinia from other centers of Etruria and produced with a non-calcareous raw material. Finally, it was hypothesized that a shift in the band associated with the asymmetric stretching of the CO_3^{2-} ion in the reflection spectra could be related to the crystal size of calcite in the ceramic paste.

The results obtained are therefore promising, even if the quality of the surface and its state of conservation can obviously influence the signal-to-noise ratio of the spectrum or determine a distortion of the bands, as was, for example, the case of one of the Etrusco-Corinthian ceramic fragments in our investigation.

In perspective, the use of external reflection IR spectroscopy can make it possible to examine in a non-invasive manner many aspects of ancient ceramic production, including the diachronic changes in production in a site, such as that of Tarquinia considered in the

present work, where the craftsmen's activity has lasted for ten centuries and, in a certain sense, continues today; or the distinction between local and imported materials, still of interest for example in the study of the Etruscan bucchero, for which a broader investigation of materials coming from different production centers and belonging to museum collections is already planned within the "Progetto Tarquinia".

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min13091211/s1>, Figure S1: External reflection FTIR spectra acquired on areas with different radius of curvature of modern ceramic vessels.

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